



# Catalytic ozonation by metal ions for municipal wastewater disinfection and simultaneous micropollutants removal

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## ABSTRACT

Several works in literature demonstrated that catalytic ozonation using metal ions promotes the decomposition of ozone and generation of hydroxyl radicals (HO<sup>•</sup>). The purpose of this study was to assess the effects of different metal ions (Fe<sup>2+</sup>, Co<sup>2+</sup> and Al<sup>3+</sup>) in disinfection of urban wastewater through *E. coli* and *Pseudomonas spp* inactivation along with cellular adenosine triphosphate (ATP) depletion. Simultaneously, the effect of catalytic ozonation of secondary effluent on the selected micropollutants removal with different ozone kinetics (acetamiprid, dichlorvos and atrazine) was evaluated in semi-continuous operation. Results demonstrated that *E. coli* and *Pseudomonas spp* inactivation increased almost 20% with 1 mg L<sup>-1</sup> Fe<sup>2+</sup>, Co<sup>2+</sup>, Al<sup>3+</sup> and 40% with 10 mg L<sup>-1</sup> Fe<sup>2+</sup> compared with single ozonation. Fe<sup>2+</sup> was the most effective metal ion on inhibiting regrowth after the treatments. The cellular ATP followed the same trend as the indicators microorganisms inactivation, with significant reduction of ATP over the treatment to single ozonation comparison. The *R<sub>OH, O3</sub>* was applied for the treatments to quantify and compare the micropollutants removal by the radical pathway. The improvement of metal ions on *R<sub>OH, O3</sub>* values occurred significantly for both stages of ozonation (before and after initial ozone demand) for all tested metals. Thus, metal ions addition to ozonation process provided an increase in simultaneous disinfection and pesticides removal as well as in the inhibition of bacterial reactivation, which resulted in savings between 30–50% of ozone dose needs compared with the same attainment in single ozonation.

## 1. Introduction

Due to the excessive population growth and rapid urbanization, especially in developing countries, there is an accelerated wastewater generation and the lack of convenient wastewater treatment plants (WWTP) and drainage facilities. This context leads to the pollution of the water resources, which makes their recycling and self-regulating capability very limited [1].

Effluents coming from inefficient WWTP may cause serious problems to human health and environment since it may contain undesirable chemical constituents and pathogens [2]. Wastewater disinfection processes must be implemented in order to achieve an effluent free of harmful microorganisms [3,4]. Besides to disinfection, attention should also be given to chemical pollutants, which have great diversity, high degree of ecosystem toxicity and are usually present in low concentrations ranging from µg/L to below ng/L [5–8]. This requires that innovative methods for wastewater treatment must continuously be explored, especially when the aim is the wastewater recycle and reuse.

Advanced oxidation processes such as ozonation have been extensively used for microorganism's inactivation [9,10] demonstrating to be an efficient technique for urban effluents disinfection, even in the inactivation of more resistant organisms than *Escherichia coli* [11,12]. Besides it appears as one of the most promising treatments for abatement of micropollutants even in low concentrations [7]. However, its reactivity toward organic pollutants is selective. Ozone reacts mainly with compounds by specific reaction pathways, denominate direct reaction with O<sub>3</sub> [13]. In contrast, the hydroxyl radical (HO<sup>•</sup>) formed by O<sub>3</sub> decomposition is a nonselective oxidant and highly reactive with organic pollutants [13,14], which promotes the complete degradation of organic pollutants, even reaching the mineralization of many micropollutants [15]. Therefore, ozone-resistant micropollutants are abated almost exclusively by HO<sup>•</sup> [16].

One of the strategies to promote greater generation of HO<sup>•</sup> is the catalytic ozonation, through the insertion of transition metals in solution (homogeneous catalytic ozonation) or through the addition of dispersed solid metal oxides (heterogeneous catalytic ozonation).

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Homogeneous catalytic ozonation mechanism follows two main pathways. The first one intensify the decomposition of ozone by the generation of the  $\text{O}_2^-$  and  $\text{O}_3^-$  radicals and subsequently  $\text{HO}^\bullet$  formation [11,17]. The other one is based on formation of complexes between the catalyst and the organic compound, followed by a final oxidation reaction [18]. Therefore, metal ions are able to enhance the removal of different organic compounds in aqueous solution, particularly those recalcitrant to direct ozone oxidation [19].

Several works on literature demonstrated that metal-catalyzed homogeneous ozonation is efficient in treating wastewater, especially concerning the oxidation of micropollutants [20–22] while others are devoted to microorganisms inactivation [23,24]. However, there are few works describing the microbial inactivation and micropollutants removal simultaneously in WWTP effluent samples [23,25].

Pesticides acetamiprid (ACMP), dichlorvos (DDVP) and atrazine (ATZ), considered as priority substances, have an uncontrolled use in several countries. These compounds call attention to the potential environment damages because these substances are persistent, toxic and able to bioaccumulate [26]. Due to the widespread employment of these pesticides, almost any water and wastewater stream contains such compounds [6,27], therefore, the removal of this type of contaminant must be effective.

ACMP and ATZ are resistant to direct oxidation by ozone [28,29], while DDVP has a medium resistance [30]. Due to variation of micropollutants reactivity with ozone, the use of kinetic models to predict micropollutants removal such as the dynamic second order kinetic-based method that includes  $\text{HO}^\bullet$  exposure ( $\int [\text{HO}^\bullet]_{dt}$ ) and total  $\text{O}_3$  exposure ( $\int [\text{O}_3]_{dt}$ ) could be used (Eq. 1), however the radicals availability remains still undetermined.

$$-\ln([MP]/[MP]_0) = k_{MP,O_3} \int [\text{O}_3] dt + k_{MP,OH^\bullet} \int [\text{HO}^\bullet] dt \quad (1)$$

The kinetic modelling of removal of pesticides in the secondary effluent is also very important as it provides details of how they behave when they undergo treatment such as ozonation. Recently, Kwon et al. [31] developed a new kinetic parameter defined as the  $\text{HO}^\bullet$  exposure per consumed  $\text{O}_3$  (Transferred Ozone Dose) (Eqs. 2 and 3).

$$R_{\text{OHO}_3} = \frac{\int [\text{HO}^\bullet] dt}{\text{TOD}_t} \quad (2)$$

$$\text{TOD} = \int_0^t \frac{F_g}{V_{liq}} \cdot ([\text{O}_3]_{in} - [\text{O}_3]_{out}) \cdot dt \quad (3)$$

where  $F_g$ ,  $V_{liq}$  represent the gas flow and the volume of the liquid phase respectively;  $t$  is the contact time; and  $[\text{O}_3]_{in}$  and  $[\text{O}_3]_{out}$  correspond to the inlet and outlet concentrations of ozone in the gas phase, respectively.

A higher  $R_{\text{OHO}_3}$  value signify a higher  $\text{HO}^\bullet$  formation, so the  $\text{HO}^\bullet$  yield from  $\text{O}_3$  decomposition for different operation conditions or different wastewaters can be easily compared using the  $R_{\text{OHO}_3}$  value, being determined through the monitoring of a  $\text{HO}^\bullet$  probe compound

during ozonation [32], which is characterized for presenting very slow direct reaction with ozone and fast reaction with  $\text{HO}^\bullet$  radicals [33], and is particularly interesting to be applied in the abatement performance prediction of ozone recalcitrant micropollutants, like the ones included in this study, through Eq. 4 [34].

$$-\ln\left(\frac{[MP]}{[MP]_0}\right) = k_{MP,OH^\bullet} \cdot R_{\text{OHO}_3} \cdot \text{TOD} \quad (4)$$

The aim of this study was to evaluate the catalytic effect of  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Al}^{3+}$  on ozone disinfection (through *E.coli* and *Pseudomonas* spp inactivation and cellular ATP depletion) and micropollutants removal (ACMP, DDVP and ATZ) in municipal wastewater samples. The catalytic ozonation effect on the inhibition of bacterial regrowth after the treatments was also studied. Finally, the influence of  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Al}^{3+}$  through the  $R_{\text{OHO}_3}$  parameter was verified along with the utility of the  $R_{\text{OHO}_3}$  concept in the modelling of the catalytic ozonation. As an  $\text{OH}^\bullet$  radical probe compound was used the ACMP, which has  $k_{\text{O}_3}$ :  $0.25 \text{ M}^{-1}\text{s}^{-1}$  and  $k_{\text{HO}^\bullet}$ :  $2.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  Cruz-Alcalde et al. [29].

## 2. Materials and methods

### 2.1. Chemicals and reagents

Acetamiprid, atrazine and 121 dichlorvos analytical standards used as target compounds, iron(II) sulphate, cobalt(II) nitrate hexahydrate and aluminium sulphate hydrate, employed as a catalysts, were acquired from Sigma-Aldrich (Germany). Pure oxygen 123 ( $\geq 99.999\%$ ) was supplied by Abelló Linde (Spain). Orthophosphoric acid and acetoneitrile were purchased from Panreac (Spain). Granu Cult™ and Chromocult® agar were acquired from Merck (Spain) and BacTiter-Glo™ Microbial Cell Viability Assay from Promega (Spain).

### 2.2. Wastewater effluent

The secondary wastewater effluent was collected from a wastewater treatment plant (WWTP) in the province of Barcelona (Spain), after an Integrated Fixed-Film Activated Sludge (IFAS) process. The different parameters of the characterization are showed in Table 1.

### 2.3. Treatment of wastewater effluents

The experiments with ozone were carried out in a 1.5 L jacketed reactor, operated in semi-continuous mode (Fig. 1), with unfiltered wastewater and carried out at the natural pH of the wastewater which was followed during the reaction (Supplementary information Table S-1).

Disinfection analysis were carried out with the indicator microorganisms naturally present in the effluent. The pesticides ATZ, DDVP and ACMP (Table 2) were spiked simultaneously to the sample and the same method was used for their analysis. For the micropollutants

**Table 1**  
Characterization of secondary effluent samples.

Parameters	Units	Values	Parameters	Units	Values
<i>E.coli</i>	CFU ( $\text{Log}_{10}$ )	$4.34 \pm 0.46$	$\text{K}^+$	$\text{mg L}^{-1}$	$42.11 \pm 1.36$
<i>Pseudomonas</i> spp	CFU ( $\text{Log}_{10}$ )	$3.46 \pm 0.21$	$\text{Na}^+$	$\text{mg L}^{-1}$	$270.28 \pm 18.2$
pH	–	$7.20 \pm 0.33$	$\text{S}^{2-}$	$\text{mg L}^{-1}$	$61.65 \pm 5.03$
Turbidity	NTU	$10.4 \pm 1.06$	$\text{Fe}^{2+}$	$\text{mg L}^{-1}$	$0.18 \pm 0.03$
$\text{UV}_{254}$	Abs	$0.40 \pm 0.05$	$\text{Al}^{3+}$	$\text{mg L}^{-1}$	–
COD	$\text{mg O}_2 \text{ L}^{-1}$	$60.75 \pm 1.02$	$\text{Co}^{2+}$	$\text{mg L}^{-1}$	–
BOD	$\text{mg O}_2 \text{ L}^{-1}$	$27.62 \pm 1.77$	$\text{Cu}^{2+}$	$\text{mg L}^{-1}$	$0.09 \pm 0.03$
TOC	$\text{mg L}^{-1}$	$16.35 \pm 10.2$	$\text{SO}_4^-$	$\text{mg S L}^{-1}$	$160.88 \pm 20.17$
TSS	$\text{mg L}^{-1}$	$68.0 \pm 0.21$	$\text{NO}_2^-$	$\text{mg N L}^{-1}$	$0.1 \pm 0.03$
Alkalinity	$\text{CaCO}_3 \text{ L}^{-1}$	$405.54 \pm 49.33$	$\text{NO}_3^-$	$\text{mg N L}^{-1}$	$0.55 \pm 0.21$
$\text{Mg}^{2+}$	$\text{mg L}^{-1}$	$40.82 \pm 5.02$	$\text{Ca}^{2+}$	$\text{mg L}^{-1}$	$118.12 \pm 7.98$

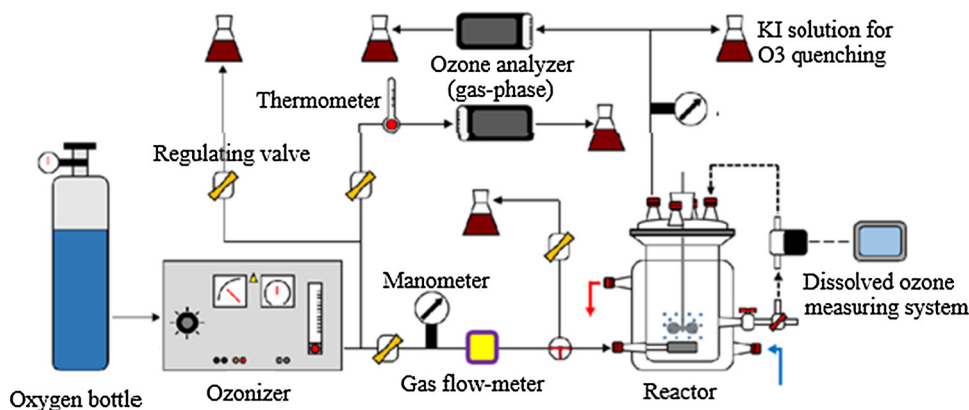


Fig. 1. Ozonation setup schematic. Adapted from [34].

**Table 2**  
Pesticides characteristics.

Pesticide	Group	Chemical formula	Structure
Acetamiprid	Neonicotinoid	$C_{10}H_{11}ClN_4$	
Atrazine	Triazines	$C_8H_{14}ClN_5$	
Dichlorvos	Chlorinated organophosphorus	$C_4H_7Cl_2O_4P$	

quantification, the linearity between the concentration of each pesticide and the area peaks were calculated and different concentrations in order to produced peaks of similar area, being 50, 200 and 100  $\mu\text{g L}^{-1}$  of ATZ, DDVP and ACMP, respectively. Blank tests were performed to assess if the target micropollutants affected the bacterial inactivation and quantification. For this, triplicate tests were done with the effluent without any type of treatment and then, the quantification of the indicator microorganisms were compared with and without contaminants.

For comparison purposes single ozonation and catalytic ozonation ( $\text{Fe}^{2+}/\text{O}_3$ ,  $\text{Co}^{2+}/\text{O}_3$  and  $\text{Al}^{3+}/\text{O}_3$ ) with 1  $\text{mg L}^{-1}$  of  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Al}^{3+}$  and 10  $\text{mg L}^{-1}$  of  $\text{Fe}^{2+}$  were carried out.

Ozone was produced by a lab ozonator (Sander, Germany) with a gas flow rate and the inlet ozone concentration maintained at 0.2  $\text{L min}^{-1}$  and 10  $\text{mg L}^{-1}$  respectively and continuously monitored by two BMT 964 ozone analyzers. For a comprehensive explanation of the ozonation system, the reader is referred to a previous publication [34].

The temperature of reaction was maintained at  $20 \pm 2^\circ\text{C}$ , under stirring conditions and samples were withdrawn at 0, 3, 5, 10, 20, 30, 40, 50 and 60 min and the microbiological parameters were immediately analyzed. The dead volume of the reactor was corrected by means of TOD calculations [33]. To ensure reproducibility the runs were repeated three times and the results were presented as average with standard deviation (SD). The Student's *t*-test was employed for comparisons in the experimental data and the significance was accepted when the null hypothesis (*p*) was less than 0.05.

#### 2.4. Analytical methods

After collection in bottles of 25 L, the samples were moved to the

laboratory and then the characterization was performed and experiments were performed with less than 1 h interval between the triplicates.

Bacterial inactivation measurements were carried out with Chromocult® TBX agar for the *Escherichia coli* bacteria count and Granu Cult™ CFC agar for *Pseudomonas spp* bacteria count. The respective agars were prepared in plates according to indications of the manufacturer and subsequently incubated for 24 h at  $40^\circ\text{C}$ . To the cellular ATP analysis, a measuring kit BacTiter-Glo™ Microbial Cell Viability Assay (Promega, Barcelona, Spain) was used. The BacTiter-Glo™ reagent containing the ATP releasing agents and the luciferase enzymes was prepared according to the manufacturer's guidelines and detected by specialized equipment (a luminometer). The data were collected as relative light units (RLU) and converted to ATP (M). Extracellular ATP was quantified by measuring ATP after filtering each sample (0.20  $\mu\text{m}$  filter). All experiments were carried out in triplicates and average values and standard deviation were plotted as colony forming units (CFU) per mL for bacteria and as  $\text{C}/\text{C}_0$  for ATP depletion.

Samples for regrowth experiments were taken from the middle to the end (25, 30 and 36  $\text{mg L}^{-1}$  of TOD) of disinfection experiments and were incubated at  $22 \pm 2^\circ\text{C}$  for 24, 48 and 72 h and plated on Chromocult® TBX agar and Granu Cult™ CFC agar, for *E.coli* and *Pseudomonas spp* bacteria count after regrowth, respectively.

The concentrations of ACMP, DDVP and ATZ were measured using a high-performance liquid chromatograph (HPLC) provided with a diode array detector (DAD) (250 mm  $\times$  4.6 mm and 5  $\mu\text{m}$  size packing) column. 35:65 volumetric mixture of acetonitrile and Milli-Q water acidified at pH 3 by the addition of  $\text{H}_3\text{PO}_4$  was the mobile phase. The flow rate was maintained at 0.7  $\text{mL min}^{-1}$ , and the detection wavelength was set to 205, 220 and 250 nm for DDVP, ATZ and ACMP, respectively. For the UV absorbance determination, a DR6000 UV VIS spectrophotometer (Hach, USA) was used.

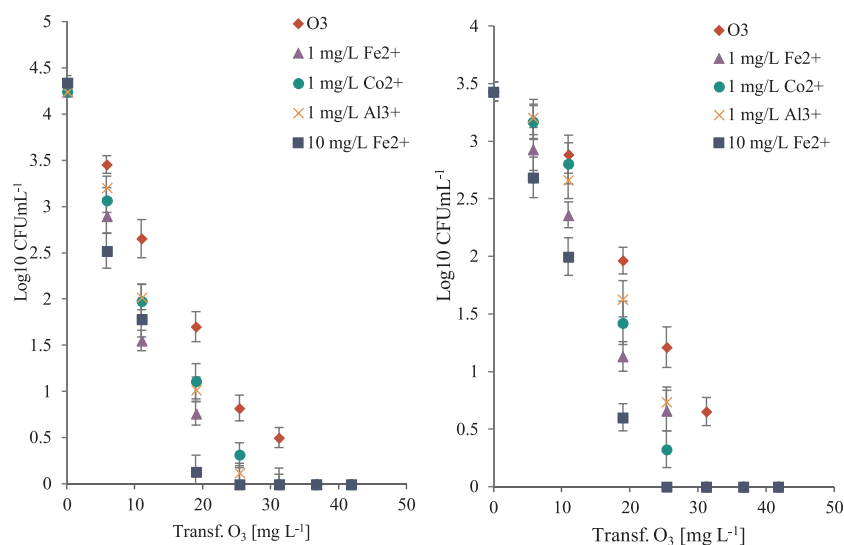
The concentration of iron in experiments performed with 10  $\text{mg L}^{-1}$   $\text{Fe}^{2+}$  was also analyzed with the purpose of verifying its possible precipitation. To quantify soluble iron, analyses of  $\text{Fe}^{2+}$  and total Fe were performed according to the 1,10-phenantroline standardized procedure (ISO 6332) by spectrophotometer Hach Lange DR 3900 at 510 nm.

### 3. Results and discussions

#### 3.1. Wastewater disinfection

The kinetic study of inactivation of microorganisms by ozone in wastewater disinfection was performed by estimating the inactivation through established mathematical model of pseudo-first order.

$$\ln\left(\frac{[N]}{[N_0]}\right) = -kt \quad (5)$$



**Fig. 2.** Disinfection of wastewater by ozonation,  $1 \text{ mg L}^{-1} \text{Fe}^{2+}/\text{O}_3$ ,  $1 \text{ mg L}^{-1} \text{Co}^{2+}/\text{O}_3$ ,  $1 \text{ mg L}^{-1} \text{Al}^{3+}/\text{O}_3$  and  $10 \text{ mg L}^{-1} \text{Fe}^{2+}/\text{O}_3$ . Inactivation of *E. coli* (A) and *Pseudomonas spp* (B).

where  $N_0$  is the number of microorganisms at time  $t = 0$ ;  $N$  the number of vital microorganisms at time  $t$ ;  $k$  the rate constant for the inactivation;  $t$ : the contact time.

The blank tests performed in presence and absence of the pesticides did not present significant statistical differences (see Supplementary information F S-2).

Fig. 2 presents the *E. coli* and *Pseudomonas spp* inactivation after ozonation of secondary effluent samples spiked with 50, 200 and  $100 \mu\text{g L}^{-1}$  of ATZ, DDVP and ACMP, respectively in absence and in presence of 1 and  $10 \text{ mg L}^{-1}$  of  $\text{Fe}^{2+}$ ,  $1 \text{ mg L}^{-1}$  of  $\text{Co}^{2+}$  and  $1 \text{ mg L}^{-1}$  of  $\text{Al}^{3+}$ . The tests performed with  $10 \text{ mg L}^{-1}$  of Co and Al are not presented, since the performance improvement compared with single ozonation was not significant for this concentration of ions (see Supplementary information F S-3).

According to Student's *t*-test, the results indicated that the *E. coli* and *Pseudomonas spp* inactivation could be enhanced by the presence of  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Al}^{3+}$  and consequently there is a synergism in the combined use of these metal ions and  $\text{O}_3$  in disinfection of real wastewaters. Inactivation of *E. coli* and *Pseudomonas spp* in the presence of metals was significantly different from single ozonation ( $p < 0.05$ ) and  $10 \text{ mg L}^{-1}$  of Fe was highly significant ( $p < 0.01$ ), as can be seen in Fig. 2 A and B.

As observed in Fig. 2A, a faster decrease in *E. coli* (CFU log10) concentration occurs after the addition of metals ions. Due to the characteristics of this effluent, the instantaneous ozone dose (IOD) is high ( $31 \text{ mg L}^{-1}$  TOD). Therefore, at the beginning of the treatment, the catalytic effect of the metals is not perceptible (see Supplementary information F S-4).

After  $20 \text{ mg L}^{-1}$  of TOD, a reduction of 3.3 and 4.2 logs of *E. coli* was observed with 1 and  $10 \text{ mg L}^{-1} \text{Fe}^{2+}$  respectively, 3.2 logs with  $1 \text{ mg L}^{-1} \text{Co}^{2+}$  and 2.8 logs with  $1 \text{ mg L}^{-1} \text{Al}^{3+}$ , while only 2.5 logs reduction was measured for single ozonation. For *Pseudomonas spp* (Fig. 2B) for the same TOD a reduction about 2.3 and 3.0 logs with 1 and  $10 \text{ mg L}^{-1} \text{Fe}^{2+}$  respectively, 2.4 logs with  $1 \text{ mg L}^{-1} \text{Co}^{2+}$  and 2.2

logs with  $1 \text{ mg L}^{-1} \text{Al}^{3+}$  were observed, while only 1.7 logs reduction was measured for single ozonation. Considering complete inactivation of *E. coli* and *Pseudomonas spp*, while single ozonation required  $36 \text{ mg L}^{-1}$  of TOD, in presence of  $1 \text{ mg L}^{-1} \text{Fe}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Al}^{3+}$  required  $30 \text{ mg L}^{-1}$  and with  $10 \text{ mg L}^{-1} \text{Fe}^{2+}$  just  $22 \text{ mg L}^{-1}$ . Positively, the presence of studied metals ions increased ozone disinfection capability, having almost doubled in the presence of  $\text{Fe}^{2+}$ .

The main consequence of this catalytic effect is the saving in energy requirements for disinfection of wastewaters. The energy costs were estimated considering operational costs related to industrial ozone production, which according to Katsoyiannis et al. has an average value of  $15 \text{ kW h}$  [34], the energy consumption is reduced from  $0.54 \text{ kW h/m}^3$  for single ozonation, to  $0.45 \text{ kW h/m}^3$  for  $1 \text{ mg L}^{-1} \text{Fe}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Al}^{3+}$  and just to  $0.33 \text{ kW h/m}^3$  for  $10 \text{ mg L}^{-1} \text{Fe}^{2+}$  representing an energy savings of almost 40% in the particular case of  $10 \text{ mg L}^{-1} \text{Fe}^{2+}$ . Based on the work of Nielsen et al. [35] which estimates  $0.0027 \text{ €/m}^3$  for  $1 \text{ mg L}^{-1}$  TOD it can be estimate the savings in euros/ $\text{m}^3$  (Table 3).

From these results it is clear that the effect of  $\text{Fe}^{2+}$  addition on the ozone oxidation efficiency becomes more significant. The results of  $\text{Fe}^{2+}$  in solution fit well with those of disinfection (Fig. 3). With initial addition of  $1 \text{ mg L}^{-1} \text{Fe}^{2+}$  disappeared from solution at  $20 \text{ mg L}^{-1}$  TOD, whereas with initial addition of  $10 \text{ mg L}^{-1} \text{Fe}^{2+}$  it was still present until  $36 \text{ mg L}^{-1}$  TOD, maintaining its catalytic improvement along the treatment. At the same time, total iron content decreased because, as  $\text{Fe}^{3+}$  was generated, it precipitated and/or coordinated with organic compounds present in the water matrix.

What must also be observed in Fig. 2 is the higher resistance of *Pseudomonas spp* to the treatment by ozone, since it have lower inactivation rate than the *E. coli* (1 log less). These results agree with bibliography [38–40], where it was also demonstrated that *E. coli* was more susceptible to the ozone disinfection compared to *Pseudomonas spp*.

All these observations are clearly reflected when compared the

**Table 3**

Estimated treatment costs per cubic meter in Euro and energy requirements in kWh for the treatments tested.

Treatment	TOD [ $\text{mg L}^{-1}$ ]	Operational costs [ $\text{€/m}^3$ ]	Energy requirements [ $\text{kWh/m}^3$ ]	Savings%
Single ozonation	36	0.097	0.54	–
$1 \text{ mg L}^{-1}$ metals ions/ $\text{O}_3$	30	0.081	0.45	17
$10 \text{ mg L}^{-1} \text{Fe}^{2+}/\text{O}_3$	22	0.060	0.33	39

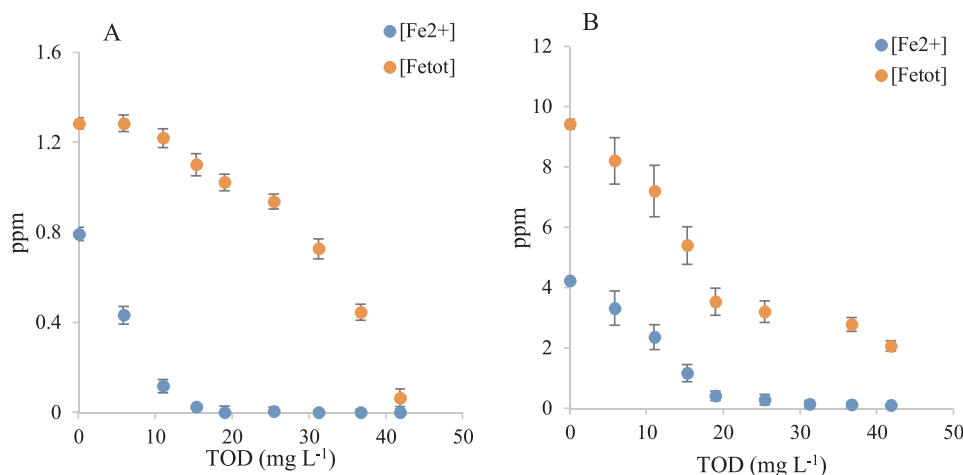


Fig. 3. Fe<sup>2+</sup> and total Fe quantification during the experiments in function of TOD. (A): 1 mg L<sup>-1</sup> Fe<sup>2+</sup>, (B): 10 mg L<sup>-1</sup> Fe<sup>2+</sup>.

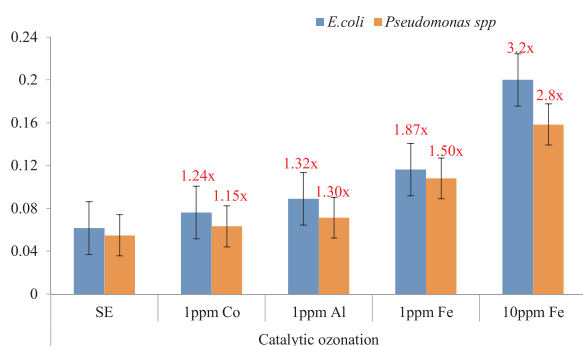


Fig. 4. Pseudo first order kinetic constants calculation for the ozonation wastewater disinfection in the presence and absence of catalysts. (SE: secondary effluent).

pseudo-first-order reaction rate constants  $k$  (min<sup>-1</sup>), as observed in Fig. 4. It seems that ozonation in presence of 1 mg L<sup>-1</sup> of Fe<sup>2+</sup>, Co<sup>2+</sup> and Al<sup>3+</sup> ions as well as 10 mg L<sup>-1</sup> of Fe<sup>2+</sup>, kinetics of disinfection for both *E. coli* and *Pseudomonas spp.* have increased significantly ( $p < 0.05$ ), between 1.2 and 3.2 times for *E. coli* and 1.15 and 2.8 times for *Pseudomonas spp.* The lower disinfection kinetics of *Pseudomonas spp.* presented in this study confirm their higher resistance to disinfection compared with *E. coli*.

The analysis of cellular ATP is used for the indirect evaluation of disinfection. It consists in the measurement of ATP, a molecule used in all cells as a carrier of free energy and phosphate groups to drive many chemical reactions. It intervenes in all the energy transactions that take place in cells and can therefore be used as an indicator for microbial activity [41].

The decline in microbial activity (as measured through cellular ATP determination) also followed the same trend as the inactivation of *E. coli* and *Pseudomonas spp.* (Fig. 5). It is noted that the addition of Fe<sup>2+</sup>, Co<sup>2+</sup> and Al<sup>3+</sup> ions to the reaction media provided a significant reduction ( $p < 0.05$ ) of ATP over the treatment compared with single ozonation.

The total elimination of cellular ATP occurred again at 36 mg L<sup>-1</sup> of TOD for single ozone, while in the presence of 1 mg L<sup>-1</sup> of metals and 10 mg L<sup>-1</sup> of Fe<sup>2+</sup> the ozone dose needed decreased to 30 and 20 mg L<sup>-1</sup>, respectively. In both methods, the CFU mL<sup>-1</sup> (log 10) and the microbial ATP cells concentration decreased with the increased of ozone dosage. Rauch et al. [42] and Shawn et al. [43] demonstrated that the ATP bioluminescence estimation and the quantitative microbiology presented high correlation.

Depending on the effluent quality, the ozone dose needed to achieve

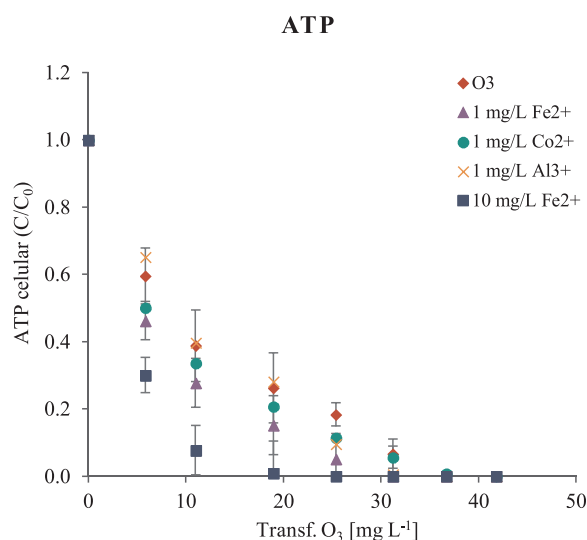
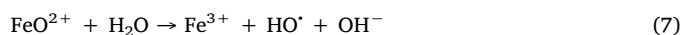


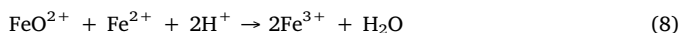
Fig. 5. Quantification of ATP cellular in function of TOD.

complete inactivation of indicator organisms varies extensively [44]. The efficiency of disinfection and pollutant removal is extremely affected when the water matrices contains large amounts of pathogens and pollutants [45]. This indicates how important it is to save ozone in the disinfection of wastewater, unlike what happens in drinking water. Reported ozone needs in literature for secondary effluents with high TSS and COD, to meet the totally indicators inactivation, such as the effluent under study, were consistently very high, from 15 to 40 mg L<sup>-1</sup> [46–49]. That represents energy requirements between 225 to 600 kW h/m<sup>3</sup>. However, in this study, the addition of 1 mg L<sup>-1</sup> of metals resulted in an economy of 17% (540 to 450 kW h/m<sup>3</sup>) and with 10 mg L<sup>-1</sup> of Fe of almost 40% (540 to 330 kW h/m<sup>3</sup>) in the ozone energy requirement (kWh/m<sup>3</sup>).

As demonstrated by Arslan et al. [36] and Saulea and Brillas [37], the decomposition of O<sub>3</sub> for hydroxyl radical's formation following a distinct mechanism when is catalysed by Fe<sup>2+</sup>. The direct reaction of Fe<sup>2+</sup> with ozone in the Fe<sup>2+</sup>/O<sub>3</sub> system resulting in the generation of HO<sup>•</sup> (Eqs (6)–(13)):

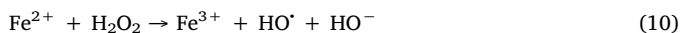


FeO<sup>2+</sup> is also able to oxidize Fe<sup>2+</sup> to Fe<sup>3+</sup>, at a slower rate, with the termination of the chain reaction:



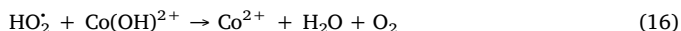
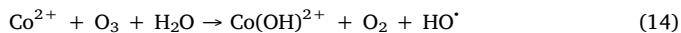
There are many mechanisms of microorganisms inactivation by ions metals which includes: deterioration in membrane cell structure or oxidation of membrane lipids, interference with cellular vital functions by the affinity for ionic metals form with sulfo-hydroxyl group inside the cell, breakage of C–N bonds, damage or destruction to several intracellular components, i.e. DNA and protein damage by reactive oxygen species generated by reduced metal cations [50–54]. However, in this study, the metal ions concentrations were very low, being far from those able to cause inhibition in the bacteria (MIC), as it can be observed in Morrison et al. [55] and Schoonen et al. [56] works.

The iron-catalysed ozonation, in addition to the Eqs. (6)–(8), can also have some common mechanisms with the Fenton process. The interaction of ozone and water is known to produce hydrogen peroxide, which may produce hydroxyl radicals [57]:



Besides to reacting directly with ozone there is evidence that metals can form complexes with compounds and generate radicals that catalyze ozonation, as can the example of Pines and Reckhow [18] for cobalt(II)oxalate/ozone (Scheme 1).

Besides complex formation, cobalt can interact directly with ozone (Eq. (14)–(16)).



There were very few studies involving  $\text{Al}^{3+}$  as a catalyst for ozonation and therefore its mechanism of action was not described. von Sonntag and von Gunten [16] report that for metals ions with both valence 2 and 3, the reactions are governed by O-transfer reactions and ozone adducts are likely intermediates.

Okawa et al. [60] found in their work that the removal rate in addition of  $\text{Al}^{3+}$  to the ozonation system was very close that with no metal ion. Al Defiery and Gopal [61] reported that with  $10 \text{ mg L}^{-1}$  of  $\text{Al}^{3+}$  no catalytic effects were found, but when adding  $100 \text{ mg L}^{-1}$  this metal exerted catalytic effect. The works cited differ from the results found in this study, since with the addition of  $1 \text{ mg L}^{-1}$  there was an increase in the generation of hydroxyl radicals ( $R_{\text{OH}}$ ) and with that, an improvement in the rate of removal of pesticides.

### 3.1.1. Bacterial regrowth

Ozone doses should decrease the concentration of pathogenic microorganisms to values that exclude any risk to human health. There are pathogenic bacteria such as *E. coli* that have a "dormancy" mechanism during wastewater treatments [62] and may then become reactive under certain conditions. In this context, in order to reuse the treated effluent, it is necessary to include a more detailed evaluation of the role

of treatment. If the treatment is not efficient, the reuse can be an agent of propagation and dissemination of pathogens. Therefore, it is very important to evaluate the regrowth capacity of the disinfection indicator microorganisms.

*E. coli* and *Pseudomonas spp.* regrowth tests were carried out at effluents treated with TODs of 25, 30 and  $36 \text{ mg L}^{-1}$  and after 24, 48 and 72 h from the completion of treatment. In Fig. 6 only  $25 \text{ mg L}^{-1}$  (A and B) and  $30 \text{ mg L}^{-1}$  (A' and B') of TODs are presented for both indicator microorganisms, because at the dosage of  $36 \text{ mg L}^{-1}$  TODs there was no regrowth in any sample for both indicator microorganisms. In the presence of both concentrations of  $\text{Fe}^{2+}$ , for the both indicator microorganisms tested, the criteria required for non-potable objectives, for instance agriculture, landscape, public parks, and golf course irrigation according to EPA was reached [63].

The metals addition had a clear inhibitory effect on the reactivation of *E. coli* and *Pseudomonas spp.* when compared with single ozonation. According to the Student's *t*-test for *E. coli*, treatments with the presence of metals differed significantly ( $p < 0.05$ ) from the single  $\text{O}_3$  tests for both 25 and  $30 \text{ mg L}^{-1}$  of TOD. However, for *Pseudomonas spp.* only treatments with  $25 \text{ mg L}^{-1}$  of TOD differed significantly ( $p < 0.05$ ) from single  $\text{O}_3$  tests.

With  $25 \text{ mg L}^{-1}$  of TOD the *E. coli* (Fig. 6A) regrowth rate decreased 4.6 times with  $1 \text{ mg L}^{-1}$  of  $\text{Fe}^{2+}$ , 2.5 times with  $1 \text{ mg L}^{-1}$  of  $\text{Co}^{2+}$  and 1.7 times with  $1 \text{ mg L}^{-1}$  of  $\text{Al}^{3+}$ , compared with single ozonation and 2.4 times with  $1 \text{ mg L}^{-1}$  of  $\text{Fe}^{2+}$  and  $\text{Co}^{2+}$  and 1.4 times with  $1 \text{ mg L}^{-1}$  of  $\text{Al}^{3+}$  for  $30 \text{ mg L}^{-1}$  of TOD (Fig. 6A'). Meanwhile, for *Pseudomonas spp.* the decreased was 2.7, 2.5 and 1.9 times for  $25 \text{ mg L}^{-1}$  of TOD (Fig. 6B) and 2.2, 1.8 and 1.6 for  $30 \text{ mg L}^{-1}$  of TOD (Fig. 6B') for  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Al}^{3+}$ , respectively.

Iron was the metal that had the greatest influence on the inhibition of both indicator microorganisms' reactivation. It is observed for the treatments with  $\text{Fe}^{2+}$  in the Fig. 6A' that  $30 \text{ mg L}^{-1}$  TOD there was no regrowth of *E. coli* and in the Fig. 6B' the regrowth of *Pseudomonas spp.* did not increase from 48 to 72 h, while for the other metals there is a minimal increase with the each analyzed time.

Kim et al. [64] and Rodrigues et al. [59] also related that  $\text{Fe}^{2+}$  can generate oxidants such as  $\text{HO}^\bullet$ ,  $\text{Fe}(\text{IV})$ ,  $\text{O}_2^-$ , and  $\text{H}_2\text{O}_2$  if oxygen is present, and these reactive oxidants generated are responsible for microorganisms' inactivation. It is also reported that these oxidants cause severe damage to integrity of cell membrane and respiratory activity.

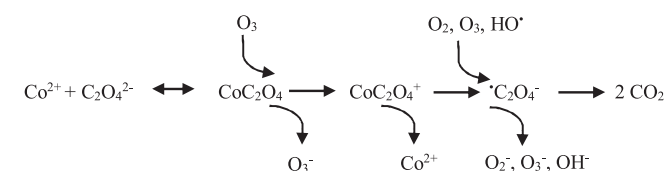
According to the purpose of reuse, it is necessary to meet the standards required in the legislation. The low regrowth rates presented, after the addition of metals, particularly Fe, would allow the treated effluent reuse in different activities, according to EPA [63], Spanish Royal Decree [65] and Brazilian legislation [66] since the regrowth rate did not reach 1 log10 for any of the treatments. This means that with only  $25 \text{ mg L}^{-1}$  of TOD ( $375 \text{ kWh/m}^3$ ) it is possible to reuse this effluent on the cited areas, representing an energy saving of almost 30% of the overall energy requirement.

### 3.2. Pesticides degradation

Another concern in recycled effluent is the removal of micro-pollutants. Fig. 7 shows the degradation of ACMP, DDVP and ATZ with single ozonation,  $\text{O}_3/1 \text{ mg L}^{-1} \text{ Fe}^{2+}$ ,  $\text{O}_3/1 \text{ mg L}^{-1} \text{ Co}^{2+}$ ,  $\text{O}_3/1 \text{ mg L}^{-1} \text{ Al}^{3+}$  and  $\text{O}_3/10 \text{ mg L}^{-1} \text{ Fe}^{2+}$ , as a function of TOD.

It can be observed in Fig. 7B that DDVP was degraded much more easily by single ozone than ACMP and ATZ (Fig. 7A and 7C), even though it is present in a concentration 2 times higher than ACMP and 4 times higher than ATZ. Comparing the pesticides kinetic constants with molecular ozone, which are listed in Table 4, it is observed that the DDVP shows moderate reactivity with molecular ozone while ACMP and ATZ are ozone-resistance compounds. On the other hand, all compounds have high reactivity with the  $\text{HO}^\bullet$ , with a magnitude order of  $10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

It is also perceived that the metals have a catalytic effect in the three



**Scheme 1.** Oxalic acid catalytic ozonation mechanism by means of the Co(II)/ $\text{O}_3$  system.

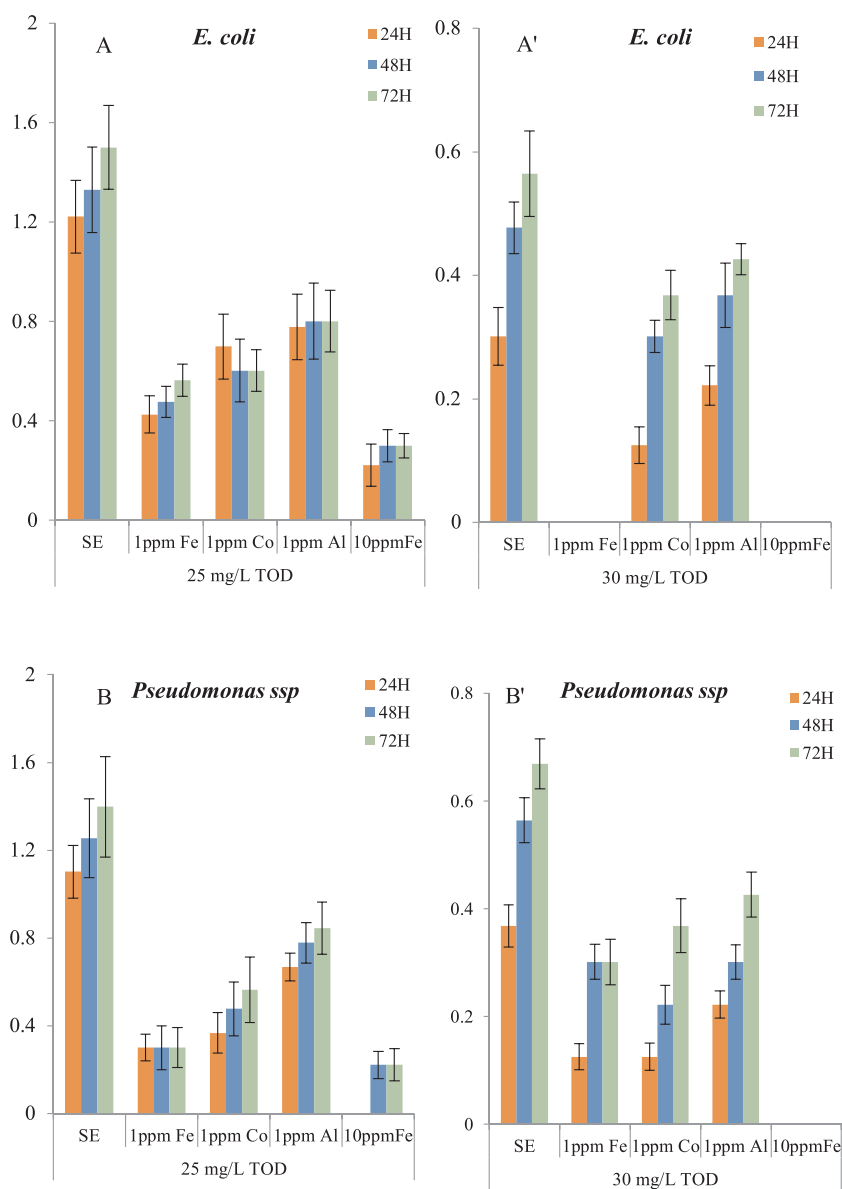


Fig. 6. Bacterial regrowth (A) *E. coli* and (B) *Pseudomonas spp* at 25 mg L<sup>-1</sup> and 30 mg L<sup>-1</sup> TODs.

pesticides removal. Thus, for each pesticide, according to the Student's *t*-test, when the means of the different treatments (absence and presence of 1 and 10 mg L<sup>-1</sup> Fe<sup>2+</sup>, 1 mg L<sup>-1</sup> Co<sup>2+</sup> and Al<sup>3+</sup>) were compared, the metals ions presence showed statistically significant differences ( $p < 0.05$ ) and this significance increased with 10 mg L<sup>-1</sup> Fe ( $p < 0.01$ ). The ACMP degradation increased between 1.45–1.66 times, DDVP increased between 2.70–5.0 times and ATZ between 1.5–2.1 times with the addition of 1 mg L<sup>-1</sup> Fe<sup>2+</sup>, Al<sup>3+</sup>, Co<sup>2+</sup> and 10 mg L<sup>-1</sup> Fe<sup>2+</sup>.

In general, when ozone is dissolved, it is consumed in two steps: first the rapid ozone consumption step which can be represented by the parameter IOD (instantaneous ozone demand) and a secondary stage characterized by a slower depletion of this oxidant. In the first stage the direct reaction to ozone predominates and in the second step (after IOD) the radical pathway, mainly hydroxyl radical predominates [32].

At the beginning of ozonation, the degradation of all pesticides was slow, since wastewater had more reacting compounds with molecular ozone, minimizing ozone decomposition into HO<sup>•</sup>. However, for TOD higher than 30 mg L<sup>-1</sup> and particularly in the presence of metals ions, pesticides depletion rates had a significant improvement ( $p < 0.05$ ). This behavior also applies to DDVP, which despite having a higher

kinetic constant with molecular ozone, had its degradation potentiated by metals as well. The micropollutants degradation enhancement was significantly increase in the presence of Fe<sup>2+</sup> ions. Again, metals ions catalyze the decomposition of molecular O<sub>3</sub> into HO<sup>•</sup>, particularly after IOD completion, causing a much faster reaction of the pesticides with HO<sup>•</sup> and consequently an overall faster degradation.

In the work of Cruz-Alcalde et al. [29] the removal of ACMP by the both possible transformation routes was analyzed, that is, direct by molecular ozone and indirect by the HO<sup>•</sup>. It was found that the degradation by means of direct reaction barely occurred, therefore the ozone decomposition into HO<sup>•</sup> is the key of ACMP removal, while another work [30] reported that both ozone and HO<sup>•</sup> can play an important role in DDVP abatement. Zhu et al. [22] compared the effect of single, homogeneous and heterogeneous catalytic ozonation on ATZ degradation and its results showed that homogeneous catalytic oxidation by leached Fe ions increased the atrazine degradation when compared with single ozonation.

From the works found in the literature dealing with catalytic ozonation and disinfection, most are involved with heterogeneous catalysis, thus this work demonstrated the importance of the catalytic effect of metals in simultaneous disinfection and elimination of O<sub>3</sub>

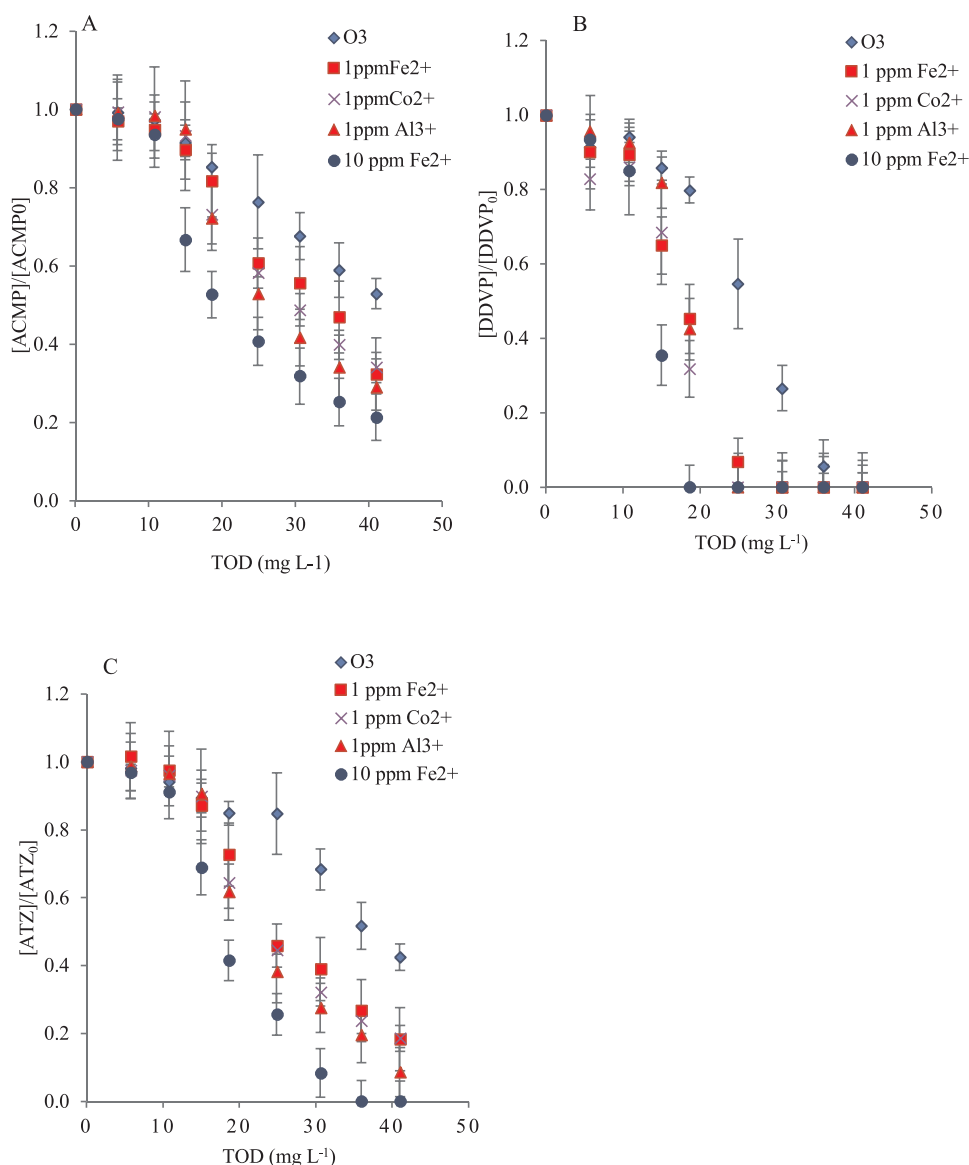


Fig. 7. Degradation of (A) ACMP, (B) DDVP and (C) ATZ.  $\diamond$   $O_3$ ;  $\square$   $O_3/1 \text{ mg L}^{-1} \text{ Fe}^{2+}$ ;  $\Delta$   $O_3/1 \text{ mg L}^{-1} \text{ Al}^{3+}$ ;  $\times$   $O_3/1 \text{ mg L}^{-1} \text{ Co}^{2+}$ ;  $\circ$   $O_3/10 \text{ mg L}^{-1} \text{ Fe}^{2+}$ .

Table 4

Kinetic constant of ACMP, ATZ, DDVP with  $HO^\bullet$  and  $O_3$ .

	$k_{O_3}$	$k_{HO^\bullet}$	References
ACMP	$0.25 \text{ M}^{-1}\text{s}^{-1}$	$2.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Cruz-Alcalde et al. [29]
ATZ	$6 \text{ M}^{-1}\text{s}^{-1}$	$3.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Acero et al. [28]
DDVP	$590 \text{ M}^{-1}\text{s}^{-1}$	$2.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Cruz-Alcalde et al. [30]

recalcitrant micropollutants.

### 3.3. Comparison of oxidation efficiency: determination of $R_{OH/O_3}$

The methodology described by Cruz-Alcalde et al. [33] was applied to calculate the  $R_{OH/O_3}$  parameter for each experimental conditions assayed. ACMP is the most ozone recalcitrant compound among the three tested pesticides (see Table 4), thus the wastewater effluent was spiked with  $100 \mu\text{g L}^{-1}$  of ACMP as  $HO^\bullet$  probe compound, and then ozonized for 60 min under the different studied operational conditions (in presence and absence of 1 and 10  $\text{mg L}^{-1} \text{ Fe}^{2+}$ , 1  $\text{mg L}^{-1} \text{ Co}^{2+}$  and 1  $\text{mg L}^{-1} \text{ Al}^{3+}$ ). Table 4 data was used to deduct the accumulated hydroxyl radical exposure according to Eq. 4. Experimental plots of

Table 5

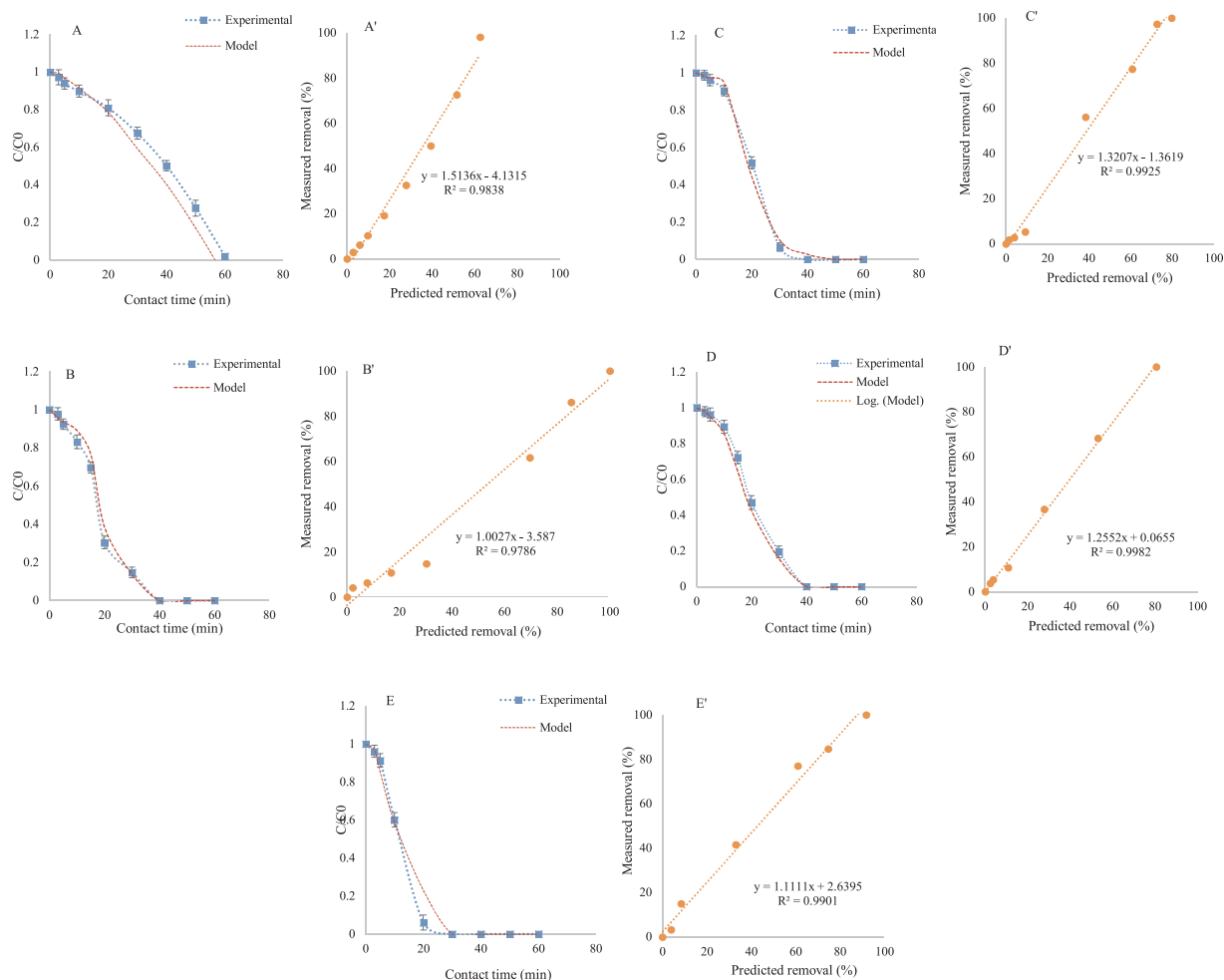
$R_{OH/O_3}$  values to 50% of ACMP degradation.

Process	$R_{OH/O_3}$	
	Stage 1	Stage 2
Single ozonation	$1.51 \times 10^{-7}$	$4.82 \times 10^{-7}$
1 $\text{mg L}^{-1} \text{ Co}^{2+}/O_3$	$2.23 \times 10^{-7}$	$9.43 \times 10^{-7}$
1 $\text{mg L}^{-1} \text{ Al}^{3+}/O_3$	$1.05 \times 10^{-7}$	$9.60 \times 10^{-7}$
1 $\text{mg L}^{-1} \text{ Fe}^{2+}/O_3$	$2.64 \times 10^{-7}$	$9.10 \times 10^{-7}$
10 $\text{mg L}^{-1} \text{ Fe}^{2+}/O_3$	$1.25 \times 10^{-6}$	$8.20 \times 10^{-7}$

\*[ACMP]<sub>0</sub> =  $100 \mu\text{g L}^{-1}$ , flow rate:  $0.2 \text{ L min}^{-1}$ ; Inlet (gas) ozone concentration:  $10 \text{ mg O}_3 \text{ L}^{-1}$  at STP conditions. First stage: before IOD ( $31 \text{ mg L}^{-1}$ ); second stage: after IOD.

$\int [HO^\bullet]dt$  versus TOD (consumed ozone, according to the employed experimental methodology) were performed to obtain the  $R_{OH/O_3}$  values for each experiment (see F S-5 in the Supplementary information). Table 5 shows the  $R_{OH/O_3}$  values resulted, which were different before (Stage 1) and after (Stage 2) IOD ( $31 \text{ mg L}^{-1}$ ).

$R_{OH/O_3}$  values increased in the second step for conditions tested as expected, which means that more hydroxyl radicals were available for



**Fig. 8.** Comparison between the experimental results and the model predictions for the ATZ removal and your correlation. (A and A': Single ozone), (B and B':  $O_3 + 1 \text{ mg L}^{-1} \text{ Fe}^{2+}$ ), (C and C':  $O_3 + 1 \text{ mg L}^{-1} \text{ Al}^{3+}$ ), (D and D':  $O_3 + 1 \text{ mg L}^{-1} \text{ Co}^{2+}$ ), (E and E':  $O_3 + 10 \text{ mg L}^{-1} \text{ Fe}^{2+}$ ).

oxidation. During early stage of ozone-based processes, there is an almost instantaneous ozone consumption exerted by  $O_3$  direct reacting matter, both organic and inorganic, present in the highly polluted secondary wastewater effluent. Once this matter is partially oxidized, this consumption decreased, increasing the ozone decomposition into hydroxyl radicals. Moreover, metals ions addition, excepting  $\text{Al}^{3+}$  (Table 5), caused a significantly increased of  $R_{OH\cdot O_3}$  values in the first stage of ozonation ( $p < 0.05$ ), particularly the presence of  $10 \text{ mg L}^{-1} \text{ Fe}^{2+}$  ( $p < 0.01$ ), although it was in the second step where all metals ions presence remarkably increased of  $R_{OH\cdot O_3}$  values.

Metals ions accelerated the decomposition of molecular ozone into hydroxyl radicals, resulting in more radical formation per transferred ozone. This increase was almost 1.8 and 8.2 times higher than the single ozonation for 1 and  $10 \text{ mg L}^{-1} \text{ Fe}$  and 1.5 times more for  $1 \text{ mg L}^{-1} \text{ Co}$  (first stage) and almost 2.0 times for all metals ions addition (second stage) (see Table 4).

It should be noted that in the second step of ozonation  $10 \text{ mg L}^{-1}$  of Fe has less effect on  $R_{OH\cdot O_3}$  values than  $1 \text{ mg L}^{-1}$ . This may be associated to the fact that the oxidation of  $\text{Fe}^{2+}$  into  $\text{Fe}^{3+}$  generated precipitates that decrease the catalytic effect of this metal (see Fig. 3). This result agrees with Kishimoto and Ueno [67] study, which  $\text{Fe}^{2+}$  appears to be associated with no significant effect in the second stage of ozonation due to the generation of precipitates throughout the treatment.

### 3.4. Prediction of micropollutants removal by homogeneous catalytic ozonation based on $R_{OH\cdot O_3}$ concept

According to the  $R_{OH\cdot O_3}$  definitions (Eq 1 and 2), the removal of the ATZ  $O_3$ -resistant micropollutant can be predicted by Eq. 4 [33]. The prediction of DDV was also performed, however it has a moderate reaction with molecular ozone, so the model underestimating the degradation of itself (Supplementary F S-6).

The experimental results and the model predictions for the ATZ removal and its correlation in the two stages for all metals tested (Fig. 8) were compared. All the experimental results presented an excellent correlation with the values of the model ( $R^2 > 0.98$ ).

It is noted that for both single ozonation and metals ions/ $O_3$ , the model can be used satisfactorily to predict the abatement efficiency of ozone-recalcitrant micropollutants. It can be seen in Figs. 8A, (single ozonation), that the model overestimated and, in the Fig. 8E ( $10 \text{ mg L}^{-1} \text{ Fe}^{2+}$ ), underestimated ATZ degradation, however these estimation deviations were not significant ( $p > 0.05$ ).

## 4. Conclusions

According to the results some conclusions are drawn as following:

- (1) The disinfection performance was improved by metals ions/ $O_3$ , as can be observed through *E. coli* and *Pseudomonas spp* inactivation and ATP cellular depletion. It was also clear that the addition of the ions to ozonation acts as a regrowth inhibitor of both indicator

microorganisms.

- (2) The improvement of metal ions on  $R_{OHO_3}$  values occurred significantly for both stages of ozonation (before and after initial ozone demand), for all tested metals.
- (3) The modelling results based on  $R_{OHO_3}$  values demonstrate that, for both single ozonation and metals ion/ $O_3$ , the atrazine depletion can be predicted satisfactory ( $R^2 > 0.97$ ), being a useful tool for the generalized prediction of ozone resistant micropollutants abatement.
- (4) Of the metal ions tested,  $Fe^{2+}$  was the one that exerted the most significant effect in both in disinfection and micropollutants removal.
- (5) The metals ions addition to the ozonation system provided saving in the ozone energy requirement ( $kWh/m^3$ ) for disinfection and pesticides abatement. To achieve 50% degradation of ACMP (most  $O_3$ -resistant compound) using  $10\text{ mg L}^{-1}$  Fe, only  $22\text{ mg L}^{-1}$  of TOD were needed, almost 50% less than that for single  $O_3$ . For the wastewater disinfection to reuse, it was necessary  $25\text{ mg L}^{-1}$  of TOD, almost 30% less than the single  $O_3$  to respect the limits of Brazilian, Spanish and American legislations. This means savings between 30–50% of total ozone requirements for the micropollutants depletion and disinfection.

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## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2019.118104>.

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